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(54) Title of the Invention: Porous Polyolefin Fiber

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SPECIFICATION

1. Title of the Invention

Porous Polyolefin Fiber

2. Claims

1. A porous fiber consisting of a polymer blend that comprises 95 to 40 wt% polyolefin and 5 to 60 wt% hydrophilic polyolefin, wherein said porous polyolefin fiber is characterized by the fact that said fiber has a porous structure in which spaces that are surrounded by lamellae and by the numerous fibrils that connect these lamellae with each other extend all the way from the fiber surfaces to the fiber central portions.

2. A porous polyolefin fiber as defined in claim 1, characterized by the fact that the contact angle of the hydrophilic polyolefin with water is 80° or lower, as measured when said polyolefin is in a film state.

3. A porous polyolefin fiber as defined in claim 1, characterized by the fact that the porous fiber has a porosity of 30 to 80%, a strength of 0.5 to 8 g/d, and an elongation of 1 to 300%.

3. Detailed Description of the Invention

Field of Industrial Utilization

The present invention relates to a porous polyolefin fiber.

Prior Art

Fibers for clothing applications and industrial material applications have become more diverse in recent years, and this diversification lead to an urgent need for fibers that are sufficiently strong yet lightweight and soft to the touch. One of the methods for reducing the weight and imparting soft hand has been to render the fibers porous. Examples include a method in which a foaming agent is blended into a thermoplastic macromolecule, the blend is spun in the molten state, and the foaming agent is decomposed at the spinning stage, yielding a porous product, as well as a method in which an extractable substance (inorganic salt, organic low-molecular compound, or

the like) is blended into a thermoplastic macromolecule, and the blend is spun and then extracted with a suitable solvent, yielding a porous product.

Problems Which the Invention Is Intended to Solve

At present, however, a method in which a foaming agent is blended, the blend is spun, and foaming is induced at the spinning stage to produce a porous product is disadvantageous in that it is difficult to produce a uniform and fine foamed structure and to obtain stable quality, and that highly porous fibers cannot be easily obtained and the stability of the spinning process is adversely affected when attempts are made to raise the porosity, because yarns frequently break and the strength markedly decreases in such cases. The extraction method is also deemed unsatisfactory because complex processes are involved, because it is difficult to completely remove the additives by extraction, and impurities tend to remain in the finished fiber product, thus affecting hand and making it difficult to obtain sufficiently good hand, and because the strength decreases markedly when attempts are made to increase porosity.

In view of this situation, the applicants have previously proposed a porous polyethylene fiber which is obtained by a method in which polyethylene is spun, heat-treated, and then drawn first in a cold state and then in a hot state, and in which spaces that are surrounded by lamellae and by the numerous fibrils connecting the lamellae with each other extend from the fiber surface to the central portion (Japanese Laid-Open Patent Application 63-158957).

Despite the fact that the base material is polyethylene, this fiber does not have the waxy feel that is characteristic of polyolefins, is lightweight, and has excellent hand. The fiber, however, is essentially hydrophobic, and because it lacks affinity for water, its use as a clothing material is inevitably limited.

To allow this fiber to be used in applications that require hydrophilic properties, attempts have been made to perform hydrophilization treatments using surfactants and other hydrophilizing agents. A resulting disadvantage, however, is that these treatments afford only temporary hydrophilic properties, which disappear when the hydrophilizing agents are removed due to contact with water. On the other hand, products obtained by spinning molten blends containing hydrophilic substances are disadvantageous because common hydrophilic substances have poor affinity for polyolefins, making it impossible to obtain fibers that deliver satisfactory performance.

Means Used to Solve the Above-Mentioned Problems

As a result of painstaking research conducted in view of this situation, the inventors perfected the present invention after discovering that blends obtained by adding polyolefins with specific characteristics to regular polyolefins can be made into highly porous, lightweight products with excellent hand and permanent hydrophilic properties by performing the same melt spinning and drawing operations as those used with common crystalline polyolefins.

Specifically, the essence of the present invention resides in a porous fiber consisting of a polymer blend that comprises 95 to 40 wt% polyolefin and 5 to 60 wt% hydrophilic polyolefin, wherein said porous polyolefin fiber is characterized by the fact that said fiber has a porous structure in which spaces that are surrounded by lamellae and by the numerous fibrils that connect these lamellae with each other extend all the way from the fiber surface to the fiber central portion.

Examples of the polyolefins that can be used in the present invention include polyethylene, polypropylene, poly(3-methylbutene-1), and poly(4-methylpentene-1). Highly crystalline compounds should be used as such polyolefins. The polymers should be selected in such a way that the undrawn yarns obtained by the melt spinning of blends containing the hydrophilic polyolefins described below have a crystallinity of 40% or higher (preferably 50% or higher) and a degree of crystalline orientation of 50% or higher (preferably 60% or higher). The hydrophilic polyolefin that is blended with the polyolefin in accordance with the present invention should be a polyolefin modified in such a way that when it is made into a film and measured, its contact angle with water is 80° or less. It is even better to use a polyolefin modified in such a way that the contact angle is 70° or less. Examples of polymers modified in such a manner include various polyolefins in which hydroxyl groups, carboxyl groups, amino groups, sulfonic acid groups, polyoxyethylene groups, and other groups are bonded to the molecular chains. Other examples include copolymers of ethylene and vinyl alcohol, copolymers of ethylene and vinyl acetate, copolymers of ethylene and maleic anhydride, copolymers in which ethylene and polyoxyethylene are chemically bonded, and polyolefins cross-linked by metal ions.

The reason that the polymers blendable with polyolefins in this case are limited to hydrophilic polyolefins is that when a hydrophilic polyolefin is blended with another polyolefin, satisfactory affinity between the two polyolefins results, so there is no

substantial impediment to the formation of a lamellar crystal structure in the undrawn yarns obtained by the melt drawing of the blend, and it is less likely that separation will occur along the interface of the components of the polymer blend. This yields the same excellent porous structure as when a polyolefin polymer alone is used. Another advantage is that because the material contains hydrophilic groups, permanent hydrophilic properties are afforded, and water and moisture can penetrate into the micropores of the fiber, thus allowing the extremely large surface area of the fiber to be utilized with high efficiency. The compounding ratio of the polyolefin and hydrophilic polyolefin should be 95 to 40 wt% polyolefin and 5 to 60 wt% hydrophilic polyolefin. This is because when a highly hydrophilic material is used as the hydrophilic polyolefin, hydrophilic properties can be obtained with a comparatively small amount of the blend, whereas when a large amount of such a hydrophilic polyolefin is blended, the formation of lamellar crystals of the polyolefins tends to be impeded, making it difficult to obtain a satisfactory porous structure and yielding poorer hydrophilic properties. By contrast, a material that has more polyolefin features must be blended in a comparatively large amount to obtain satisfactory hydrophilic properties. Even when large amounts of materials are blended, the combination should be 90 to 50% polyolefin and 10 to 50% hydrophilic polyolefin. It is unsuitable for the polyolefin ratio to be lower than the aforementioned lower limit or higher than the aforementioned upper limit, because in the first case it becomes more difficult to obtain a sufficiently uniform porous structure, and in the second case the hydrophilic properties become inadequate.

Because the porous fiber of the present invention has a porous structure that is obtained by drawing undrawn hollow yarns (fabricated by spinning crystalline macromolecules) and stretching the molecules folded between the lamellae of the undrawn yarns to cleave said molecules into fibrils, spaces form around the numerous fibrils that are oriented along the fibers and that connect the lamellae with each other, and this structure stretches from the fiber surfaces to the fiber central portions because it remains almost the same all the way from the fiber surfaces to the central portions. The surface area of the fiber is therefore very large, and the porous structure extends up to the fiber central portions, yielding excellent hand (in contrast to fibers in which the surface alone is roughened).

The porous structure of the present invention should have a porosity of 30 to 80%, a strength of 0.5 to 8 g/d, and an elongation of 1 to 300%. When the porosity is

lower than the aforementioned lower limit, weight increases proportionately and hand becomes unsatisfactory, whereas when the porosity exceeds the upper limit, strength tends to decrease. Taking into account clothing applications, strength and elongation should fall within the aforementioned range.

A method for manufacturing the porous fiber of the present invention will now be described.

The aforementioned polyolefin and hydrophilic polyolefin are first blended, and the blending operation must yield a sufficiently uniform blend. The aforementioned polymers should therefore be blended in advance using, for example, a blender such as a V-type blender, or blended in the molten state in a melt extruder and then pelletized, and the pellets introduced into an extruder for melt spinning. The blend is melt-spun using a common spinneret for fiber spinning to produce crystalline undrawn yarns. In this case, melt spinning operations performed with the use of a slow cooling zone (length: 1 to 3 m; atmosphere temperature: 50 to 100°C) located directly beneath the spinneret are preferred because they yield undrawn yarns with higher crystallinity. The formation of the lamellar structure proceeds unsatisfactorily when the undrawn yarns have a crystallinity of less than 40% or a degree of crystalline orientation of less than 50%. The operations described below fail to produce a porous structure in this case. Even when produced, the porous structure is nonuniform and does not contain portions extending all the way from the fiber surface to the fiber central portion, making it impossible to obtain the highly porous material that is the object of the present invention.

The spinning temperature should be at least 20°C higher than the melting point (hereinafter " m_{pH} ") of the highest-melting polymer (of the polymers comprising the blend) but no more than 80°C higher than said melting point (m_{pH}). It is unsuitable to perform spinning at a temperature lower than the lower limit of this temperature range, because although the resulting undrawn yarns are highly oriented, the maximum draw ratio attainable during the subsequent drawing process for fabricating a drawn porous material is lowered, and a sufficiently high porosity is difficult to obtain. Nor is it desirable to perform spinning at a temperature that exceeds the upper limit of the aforementioned temperature range, because in this case high porosity is difficult to obtain as well. The spinning draft should be 200 to 10,000, and preferably 200 to 5000. Molten yarns received at such a high draft can form lamellae consisting of highly oriented lamellar crystals inside the undrawn yarns, and thus yield yarns with a

highly porous structure during the subsequent drawing process. It is unsuitable for the slow cooling zone to be shorter than 1 m or to have an atmosphere temperature below 50°C, because in this case yarns often break directly beneath the spinneret, and process stability tends to decrease. No is it suitable for the slow cooling zone to be longer than 3 mm or to have an atmosphere temperature above 100°C, because in this case yarn cooling becomes unsatisfactory, and the draft is apt to decrease substantially, impairing the crystallinity and orientation of the resulting undrawn yarns.

The undrawn fiber thus obtained can be drawn without undergoing any additional treatments, or it can be drawn after being annealed under constant-length or relaxation conditions at a temperature which does not exceed m_{pH} and falls within a temperature range within which the structure of the undrawn yarns is hardly damaged at all.

The porous fiber of the present invention is obtained by drawing the undrawn yarns thus obtained and rendering them porous. Drawing should be a combination of cold drawing (at a temperature ranging from $m_{pH} - 80^\circ\text{C}$ or lower to $m_{pH} - 220^\circ\text{C}$ or higher, and preferably $m_{pH} - 160^\circ\text{C}$ to $m_{pH} - 90^\circ\text{C}$) and subsequent hot drawing (at a temperature ranging from $m_{pH} - 60^\circ\text{C}$ to $m_{pH} - 5^\circ\text{C}$). The hot drawing may be a multistep drawing operation consisting of two or more steps. Cold drawing, which is an important process for manufacturing the fiber of the present invention, involves forming microcracks in the noncrystalline portions between the lamellar crystals of the highly oriented, crystalline undrawn yarns. These cracks are expanded by performing thermoplastic transformation and drawing operations during the subsequent hot drawing process, yielding the specific porous structure described above. The draw ratio of cold drawing should be 5 to 100%, and the draw ratio of hot drawing should be set in such a way that the combined draw amount of cold drawing and hot drawing is 100 to 700%. When the hot drawing temperature is higher than $m_{pH} - 5^\circ\text{C}$, the fibers become transparent, and the desired porous structure cannot be obtained. It is unsuitable for the hot drawing temperature to be lower than the aforementioned lower limit because porosity decreases with a reduction in temperature. A total draw amount that exceeds 700% is unsuitable because of frequent yarn breakage during drawing. Hot drawing endows the porous polyolefin fiber thus obtained with substantial shape stability, although heat setting may also be performed as needed at a temperature ranging from $m_{pH} - 60^\circ\text{C}$ to $m_{pH} - 5^\circ\text{C}$ under conditions of stretching or limited relaxation.

Practical Examples

The present invention will now be described in further detail through practical examples. In these practical examples, the crystallinity of polymer blends was determined by integrating the refraction intensity in all directions using a wide-angle x-ray diffraction apparatus, and calculating the crystallinity using the following formula.

$$\text{Crystallinity } \chi_c = (\text{Integral of total diffraction intensity} - \text{Integral of diffraction intensity of noncrystalline portion}) / \text{Integral of total diffraction intensity}$$

In addition, the degree of crystalline orientation was determined by first calculating the half value of the distribution of the diffraction intensity of the (110) plane along different fiber axes using a wide-angle x-ray diffraction apparatus, and then calculating the degree of crystalline orientation using the following formula.

$$\text{Degree of crystalline orientation} = (H_{(110)} / (180 - H_{(110)})) \times 100 (\%)$$

In the formula, $H_{(110)}$ is the half value of the (110) plane.

The contact angle with water in a film state was measured by a known method using a Kyowa Contact Angle Meter manufactured by Kyowa Kagaku.

Practical Example 1

A high-density polyethylene ("Hi-Zex 2200J," manufactured by Mitsui Petrochemical) with a density of 0.968 g/cm³ and a product ("Hi-Miran-1702"; manufactured by Mitsui Polychemical; contact angle with water when made into a film: 69°) obtained by cross-linking a copolymer of polyethylene and acrylic acid with zinc ions were dried after being blended in a 1:1 ratio in a V-type blender. The blend was wound after being spun through a 36-hole nozzle with a hole diameter of 0.6 mm at a spinning temperature of 200°C and a spinning rate of 300 m/min.

The resulting undrawn yarns were heat-treated for 120 seconds at 115°C under conditions of constant length. The undrawn yarns had a crystallinity of 62% and a degree of crystalline orientation of 75%. These undrawn yarns were first cold-drawn to 80% at 25°C and then hot-drawn in a heating box (heated to 115°C) with a length of 2 m until the total draw ratio reached 520%. Relaxation and heat setting were then

performed in a heating box (with a length of 2 m heated to the same temperature) in such a way that the total draw ratio was 400%.

The resulting porous fiber had a porous structure in which spaces that were surrounded by lamellae and by the numerous fibrils that connected these lamellae with each other extended all the way from the fiber surfaces to the central portions. The fiber was very soft to the touch; its porosity, strength, and elongation were 66.8%, 4.85 g/d, and 38.9%, respectively.

1 g of this porous polyethylene fiber was subsequently dipped for 1 hour in 200 cc of ion-exchange water and then dehydrated for 5 minutes in a centrifugal separator at 1000 rpm. The weight increase ratio was measured, and the water content calculated. The result was 76%.

As a comparative example, porous polyethylene was produced in the same manner as above, but using only the high-density polyethylene with the density of 0.968 g/cm³. The water content was measured and found to be 6%.

Practical Example 2

A high-density polyethylene ("Hi-Zex 2200J," manufactured by Mitsui Petrochemical) with a density of 0.968 g/cm³ and an ethylene-vinyl alcohol copolymer ("Soanol D"; manufactured by Nippon Synthetic Chemical; contact angle with water in a film: 56°) were dried after being blended in a 7:3 ratio in a V-type blender. The blend was wound after being spun through a 36-hole nozzle with a hole diameter of 0.6 mm at a spinning temperature of 200°C and a spinning rate of 300 m/min.

The resulting undrawn yarns were heat-treated for 120 seconds at 115°C under conditions of constant length. The undrawn yarns had a crystallinity of 68% and a degree of crystalline orientation of 82%. These undrawn yarns were first cold-drawn to 80% at 25°C and then hot-drawn in a heating box (heated to 115°C) with a length of 2 m until the total draw ratio reached 520%. Relaxation and heat setting were then performed in a heating box (with a length of 2 m heated to the same temperature) in such a way that the total draw ratio was 400%.

The resulting porous fiber had a porous structure in which spaces that were surrounded by lamellae and by the numerous fibrils that connected these lamellae with each other extended all the way from the fiber surfaces to the central portions. The

fiber was very soft to the touch; its porosity, strength, and elongation were 52.4%, 2.40 g/d, and 109%, respectively.

The water content of this fiber was measured in the same manner as in Practical Example 1 and was found to be 62%.

Merits of the Invention

As described above, the porous polyolefin fiber of the present invention has a porous structure in which spaces that are surrounded by lamellae and by the numerous fibrils that connect these lamellae with each other extend all the way from the fiber surfaces to the fiber central portions, and thus has a large surface area, is very lightweight, has soft hand, is white without being transparent, and has excellent mechanical characteristics despite being highly porous. Unlike materials rendered porous by extraction with solvents or the like, the proposed fiber is rendered porous by drawing alone, and is a hygienic material devoid of solvents, extraction additives, or the like. In addition, said fiber is permanently hydrophilic, and therefore readily absorbs perspiration and is ideal as a fabric material for medical applications and for underwear and other types of clothing that come into direct contact with the skin. The substantial water content and intrapore hygroscopicity can be used in various industrial material applications.